DEPARTMENT OF CERAMIC ENGINEERING

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

.SYNTHESIS AND CHARACTERIZATION OF CORDIERITE BASED GLASS-CERAMIC

SUBMITTED BY

SOUMYA SOURAV PATRA

(110CR0103)

(Under the guidance of Prof. Arun Chowdhury)

In the partial fulfillment of the requirements for the degree

Of Bachelor of Technology

NATIONAL INSTITUTE OF TECHNOLOGY

ROURKELA

CERTIFICATE

This is to certify that the thesis entitled, "synthesis and characterization of cordierite based glass-ceramic." submitted by Mr. Soumya Sourav Patra (Roll no - 110CR0103) in partial fulfillment of the requirements for the award of Bachelor of Technology Degree at Ceramic Engineering in National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other university / institute for the award of any Degree or Diploma.

Prof. Arun Chowdhury

Department of Ceramic Engineering

National Institute of technology

Rourkela-769008

ACKNOWLEDGEMENT

With deep respect, I avail this opportunity to express my gratitude to Prof. Arun Chowdhury Department of Ceramic Engineering, National Institute of Technology, Rourkela for his inspiration and guidance and valuable suggestion throughout this research work. His vast knowledge in the field of Science and Technology helped to enlighten me. It would have been impossible on my part to come out with this project report without him. I would like to thanks to the HOD, Ceramic Department and all other faculties for their support and valuable suggestions throughout this research project. I would also take this opportunity to express my gratitude to the non-teaching staff for their help and kind support at various stages of work.

I am also thankful to the Research Scholar in the Department of Ceramic Engineering for helping out in labs and analysis. And lastly I am thankful to my parents and friends for their constant support.

Soumya Sourav Patra

Roll No - 110CR0103

ABSTRACT

Cordierite glass-ceramic sample were made using with rice husk ash as the source of silica. Three different nucleating agent were introduced in the base glass composition - TiO_2, ZrO_2, and ZrO_2-TiO_2 in (1:1) proportion by weight. After preparation of these cordierite based glass-ceramic phase evaluation was studied in the temperature range 1250 to 1350^oC. XRD and electron microscopy were employed to characterize all heat treated specimens. Linear thermal expansion behavior of the glass-ceramic samples was studied with the help of dilatometer. For hardness testing Vickers's method was adopted.

CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

INTRODUCTION

INTRODUCTION

Cordierite is mainly a ceramic material of magnesium aluminum silicate having formula $2Mgo2Al_2O_35SiO_2$. It resembles to hexagonal form of structure (cyclosilicate sheet). It is commonly prepared by oxide powder sintering. Cordierite based glass-ceramics have many attractive properties. This type of material is very good at thermal shock resistance, thermal stability and excellent dielectric property. Cordierite is also called as indialite. Cordierite was discovered in 1813 and is named after the French geologist Louis Cordier (1777-1861). In cordierite three types of basic component are present they are MgO, Al_2O_3, SiO_2. In glass-ceramic technology we can select the composition to optimize the viscosity of the glass and achieve advantageous processing. As cordierite is co-fired with copper at low temperature (below 1000 ^oC). So it became popular than aluminium nitride. The sintering temperature range of cordierite is close to the melting temperature. Sometimes research groups encounter some difficulties to sinter the cordierite product. By adding sintering aid we can get good mechanical properties along with high dielectric constant and high thermal expansion.

Properties	**Cordierite**
Chemical formula	$2MgO.2Al_2O_3.5SiO_2$
Density	2.60 g/cc
Modulus Of Rupture	117 MPa
Young's modulus	70 GPa
Thermal expansion coefficient	1.7 (x10-6/°C)
Thermal Conductivity	3 W/m K (room temp.)
Max. Operating temp.	1371 °C
color	Gray, white, blue

Table 1 - Physical and mechanical properties of cordierite

In order to develop glaze fully, layer flux are added which matures the glaze layer. So that glaze should have suitable surface tension and thus crawling effect is minimized. To control crystallization some nucleating agents are added. By using nano-sized silicon powder and increasing surface area. Formation of silicon nitride becoming will increase which should be related to Si_3N_4 formation at low temperature and prevent to reacting with cordierite to form liquid form during sintering. Thermodynamically cordierite exists in two phase's α-cordierite (high temperature phase, stable) μ-cordierite (low temperature phases)

Advantage of cordierite glass ceramic	**Disadvantage of cordierite glass ceramic**
High thermal shock resistance	Low mechanical property
Low dielectric constant & loss	Narrow sintering temperature
Low thermal expansion	Dense cordierite preparation is difficult
High thermal stability	Monophasic cordierite preparation is difficult
High chemical stability	Without sintering aid cordierite ceramic preparation is not possible
Can be co-fired with copper below1000^o c	By adding sintering aid its thermal expansion and dielectric constant and dielectric loss increases

Table- 2 advantage and disadvantage of cordierite glass ceramic:

APPLICATION

Catalytic converter are mainly made of from ceramic containing a large proportion of synthetic cordierite. The manufacturing process deliberately aligns the cordierite crystal to make use of the very low thermal expansion seen for the axis this prevent thermal shock cracking from taking place when the catalytic converter is used .cordierite is use in electronic circuit ,as a capacitance due to low dielectric constants of cordierite. Cordierite is also used in

refractory hot plate, randomness and electronic circuit substrates, kiln furniture, gemstone, Industrial heat exchanger for gas turbine engine. Cordierite is also use to make MLCI (multilayer chip inductor) capacitor. By controlling thermal barrier we can use cordierite in space application.

CHAPTER 2

LITERATURE REVIEW

In order to decrease the cost of production of cordierite Milan Kanti Naskar [1] used agro-based waste material such as rice husk ash, Fumed silica and Tetraethaylorthosilicate (TEOS) as a source of silica. They found that rice husk ash is abundantly available and it is an agricultural waste by using rice husk ash for cordierite preparation the product will be less costly and environment friendly. In rice husk ash silica crystallization of α-cordierite takes place through the intermediate phases of cristobalite and $MgAl_2O_4$ spinel but it occurs via the intermediate phases of $MgAl_2O_4$ Spinel and μ-cordierite for Tetraethaylorthosilicate (TEOS) source and $MgAl_2O_4$spinel for fumed silica. In rice husk ash silica source wide size distribution of the particles was found. By using SEM they found that these three sources of silica show agglomerated and irregular morphology. From FTIR study they get the idea of characteristic bands of Si–O–Si symmetric and asymmetric stretching vibration in SiO_4 tetrahedral, Al–O bonds in AlO_6 octahedral and AlO_4 tetrahedra for the powders obtained from three different sources of silica at different calcination temperatures. From this literature I decided to use rice husk ash silica as a silica source for preparation of cordierite based glass-ceramic because these are easily available and less costly than other source of silica.

Effects of (P_2O_5, B_2O_3) Additives on Phase-Transformation Kinetics and Microstructural Development of Stoichiometric Cordierite Glasses were studied by Shiang-Po Hwang and Jenn-Ming Wu [2] they found that additive like B_2O_3 and P_2O_5 influences α-cordierite formation but it affect μcordierite drastically. Heterogeneous nucleation of μ-cordierite occurs at the impurities on the parent surface and forms spherulitic dendritic structure. B_2O_3 additive produces dendritic arm and inter-dendritic interface between residual glass and μ cordierite.P_2O_5 increases the growth of μcordierite and change to interface controlled from diffusion controlled and it removes dendritic nature of μcordierite and helps in transforming to

hexagonal crystal structure. There are two types of phase transformation of α-cordierite. In 1st case nucleation of α-cordierite occurs between inter-dendritic residual glass and μcordierite dendritic arms interface. In this growth of α-cordierite takes place at the expense of glass matrix and interdendritic residual glass. Growth rate increases when density of interfacial area between residual glass and μ-cordierite increases. In 2nd case formation of α-cordierite occur by transforming μcordierite that are formed earlier. Transformation rate will be quicker when μcordierite dendritic arm will be thinner. So P_2O_5 decreases α-cordierite but B_2O_3 increases or enhances α-cordierite. Temperature effect less in P_2O_5 than in B_2O_3 because growth rate of μ-cordierite is less than α-cordierite when we increase temperature.

Sintering and Crystallization property of sol gel prepared cordierite was studied by Rada Petrovic [3]. He studied that by using the raw material; like Al_2O_3 salt, magnesium and silicic acid can decrease the cost of preparation of cordierite by sol –gel preparation method. In sol gel method we have higher control over quality of cordierite but in sol- gel processing raw materials are very costly. At 800°c viscous sintering takes place without crystallization of μcordierite. At 900°c single phase μcordierite gel is formed. At 1200 °C μ-cordierite transform to α-cordierite initiated. At 1300 °C, μ to α-cordierite transformation completed and sinteribility is more than in 800°C. μ-cordierite crystallization is interfacial controlled crystallization having constant nuclei number with surface nucleation which decreases the activation energy than volume nucleation. The main reason of surface nucleation occurs due to the viscous sintering which causes shrinkage so nucleation occur at the surface. From this they observe that hard agglomerates occurs at calcination temperatures where viscous sintering takes place without crystallization than in the case where a crystallized powder was obtained. But this sol gel processing cannot use industrially because it is a complicated process and takes lot of time.

Effect of K_2O and CeO_2 were studied by Zhi Ming Shi [4]. He observed that sintering additive which include rare earth mineral are important for cordierite glass ceramics. Oxides which have low melting temperature forms liquid phage which helps in sintering and transformation of cordierite. K_2O and CeO_2 helps in the formation of cordierite by influencing or increasing the reaction of cristobalite. K_2O is less effective than CeO_2 to eliminate spinel phases. The cordierite glass ceramic batch having 2 weight percentage of K_2O cannot use to prepare high quality glass ceramic because at low temperature sintering the glass contain large quantity of glass and spinel phases. The cordierite glass ceramic batch having 4.0 or less than 4.0 weight percentage of CeO_2 contains little amount of glassy phase and cordierite when sintered at temperature 1450 ^oC for 3 hours. So it is very good for the production of commercial cordierite glass ceramic because it contain large quantity of cordierite and it has low linear thermal expansion K_2O and CeO_2 removes the interphase which is attached to the physicochemical properties of the K^+ and Ce^{4+}ions. K_2O and CeO_2 removes spinel in different route. CeO_2 restricts Al_2O_3 and MgO reaction to produce spinel phase. K2O helps spinel to dissolve into liquid phase. But both K_2O and CeO_2 increases the chemical reaction between cristobalite with Al_2O_3 and MgO.

Effect of manganese doping on cordierite was studied by Yu. V. Baschenko [5]. He showed that when magnesium partially replaced by manganese in the region of the formation of solid solution with cordierite structure. Then it makes the, fracture resistance, thermal shock of cordierite based glass ceramic 250-300^o c higher. The increase in thermal shock resistance is due to reduction of the thermal coefficient of linear expansion. But doping of manganese on cordierite has no effect on strength and fracture toughness. The increase in manganese content

makes the structure micro strain of the cordierite crystal lattice smaller. So magnesium should replace by manganese of only 50 weight percentage.

Cordierite glass ceramic containing ZnO was observed by Guo-Hua Chena [6]. He observe that replacement of Al_2O_3 by ZnO decreases the melting temperature and crystallization temperature of glass ceramics. The glass transition temperature firstly decreases and then increases. So ZnO should be in the range of 8 weight percentage. After complete sintering the fully dense glass ceramic with crystalized α-cordierite, gahnite was successfully fabricated at relative low temperature. Superior and reliable properties such as low thermal sinteribility, thermal expansion coefficient, flexural strength and dielectric property at 1 MHz is obtained by adding ZnO.

Cordierite based glass ceramic processed by tape casting studied by Jose´ Maria F. Ferreira [7].They showed that cordierite glass green tapes were successfully fabricated via aqueous tape casting. The viscosity of the suspensions increase with solid content whereas the apparent yield stress (T_g) as well as the shear stress required for making the system to flow with increasing shear stress value required for making the system to the flow with increasing shear rates became more pronounced with decreasing mean particle size of the glass powder component. The calculated max solid loading of the suspension was 70%. When the mean particle size of glass and cordierite were about 4.8 and 0.8 micron meter. Homogeneous and dense substrate can be achieved when the solid content was about 85 wt% and particle size ratio between glass and cordierite was about 5.2. The dielectric constant of the sintered bodies at 1150^{o}C /2hr was around 5 and the dissipation factor was about 0.01 at 1 MHz.

Cordierite based glass ceramic processed by slip casting is observed by J.M.F Ferreira [8]. From his experiment he conclude that amount of dispersant and solid loading play an important role on rheological behavior of cordierite-glass suspension. At low solid loading

(50wt %) shear-thinning behavior can be observed, irrespective of the amount of dispersant, within the whole range of shear rate. As the solid shear thickening in the higher shear rate range, especially for the dispersant concentration that gave the viscosity values. For all solid loading green density increase with increasing amount of dispersant up to an optimal value, decreasing afterwards, on the other hand, the size of pores decrease and the pore size distribution became more uniform with increasing amount of dispersant up to an optimal level, while the volume fraction of pores tends to increase for the further amount of dispersant. Slip casting proves to be more effective processing technique to prepare dense and homogeneous cordierite based glass ceramic composites compared to the dry processing technique.

OBJECTIVE

- To utilize one of the agricultural waste (amorphous silica) in developing thermally stable cordierite glass-ceramic.
- To synthesize glass-ceramics employing TiO_2, ZrO2 and TiO_2 along with ZrO_2 separately to do a comparative study in phase evaluation.
- To correlate the bulk density, thermal expansion behavior and mechanical property with microstructure.

CHAPTER - 3

EXPERIMENTAL

[4.1] Raw material required

The raw materials used for making cordierite glass ceramic are:

- Rice husk for silica
- Reactive alumina
- Magnesium carbonate for magnesia
- Titanium dioxide (nucleating agent)
- Zirconium dioxide (nucleating agent)
- Arsenic trioxide (homogenizer)
- Boric acid (fluxing agent)

[4.2] Preparation of silica from rice husk

i. Rice husk was washed with water for 5-6 times thoroughly.

ii. Then it was allowed to dry.

iii. Then the dried husk is taken in batches of 50 gm and for each batch 375 ml of water and 125 ml of hydrochloric acid is taken and proceed for leaching process.

iv. Leaching is mainly done to remove sodium, potassium, calcium ion present in the husk.

v. Water and hydrochloric acid is mixed in a beaker and heated.

vi. When it starts to boil 50 gm of the husk was added into it. Boiling is continued, till a chocolate brown color is seen and level of H_20 and HCl should be maintained throughout the heating process.

vii. Now add boiling water to the leached rice husk and then rinse the water out, the process is continued until a PH 7 is obtained.

viii. These rice husk are dried and then calcined at 700^oC for a soaking period of 4 hour.

ix. Rice husk chars off leaving behind silica.

x. The rice husk ash silica is grinded with the help of mortar and pestle.

[4.3] Preparation of zirconium dioxide (nucleating agent)

Zirconia (ZrO_2) is prepared by precipitation reaction with zirconium oxychloride with sodium hydroxide.

i. Zirconium oxychloride solution is prepared by adding zirconium oxychloride powder into a beaker and then water is added to make the solution.

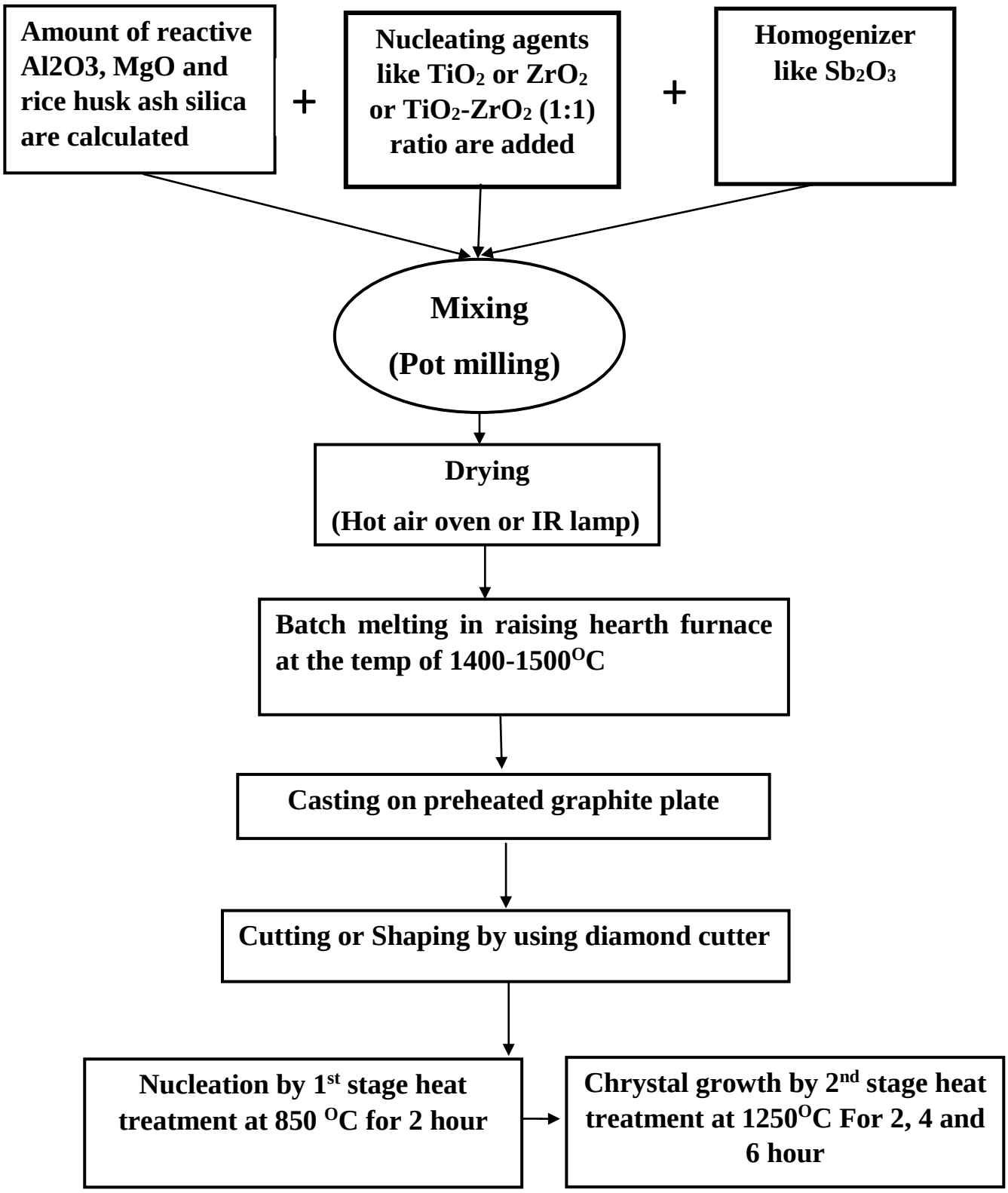
ii. These Zirconium oxychloride solution is added to the sodium hydroxide solution in a drop wise manner with the help of dropper.

iii. Addition of zirconium oxychloride forms jelly like substance. These jelly are filtered by using filter paper.

iv. After filtration these jelly are washed with boiled water to make Ph 7-6.

v. Then it is dried under IR lamp to remove water and zirconium hydroxide converted to zirconium dioxide. If the agglomeration occur then these ZrO_2 should be pot milled.

[4.4] Flowchart for cordierite based glass-ceramic preparation



[4.5] Batch preparation of cordierite based glass ceramic

Raw material	Weight in gm
Rice husk ash Silica	24.79 gm
Reactive Alumina	14.25 gm
Magnesia Oxide	6.65 gm
Titanium Dioxide	5.35 gm
Antimony Trioxide	0.25 gm
Boric acid	0.00 gm

Table 3 Batch -1 for TiO2 nucleated cordierite glass-ceramic

Raw material	Weight in gm
Rice husk ash Silica	23.55 gm
Reactive Alumina	14.25 gm
Magnesia Oxide	6.65 gm
Titanium Dioxide	3.2 gm
Zirconium dioxide	2.15 gm
Antimony Trioxide	0.25 gm
Boric acid	3.5 gm

Table 4 Batch-2 for TiO_2 and ZrO_2 (mix) nucleated cordierite glass-ceramic

Raw material	Weight in gm
Rice husk ash Silica	23.55 gm
Reactive Alumina	14.25 gm
Magnesia Oxide	6.65 gm
Zirconium dioxide	6.1 gm
Antimony Trioxide	0.25 gm
Boric acid	3.5 gm

Table no 5 Batch-3 for ZrO2 nucleated cordierite glass-ceramic

[4.6] Cordierite based glass-ceramic preparation

50.0 gm batch was prepared by using rice husk ash silica, Reactive alumina, magnesium oxide, antimony trioxide, nucleating agents like TiO_2 or ZrO_2 or TiO_2- ZrO_2(1:1) ratio and boric acid in place of soda ash (if required).

Here antimony trioxide Sb_2O_3 act as a homogenizing agent which helps in homogenization of glass melt. Boric acid is also use as a fluxing agent which decreases the melting temperature of ZrO_2 and TiO_2- ZrO_2 batch melting.

The batch is thoroughly mixed through pot milling for 24 hr by using propanol. After that it is dried with the help of electric oven or IR lamp and crushed with the help of agate mortar. Then the crushed powder are poured in 100ml Sillimanite crucible and melting is done in a raising heart furnace at the temp of 1400 ^{O}C for TiO_2 nucleated sample and 1500^{O}C for ZrO_2 and TiO_2- ZrO_2 nucleated sample for 2 hour soaking time at the rate of 2^{O}C /min. when melting is complete then molten glass is poured on a preheated graphite plate. After 2 hour when it became partly cooled then it is transfer to pit furnace for annealing at the temperature of 600^{o}C.Then it is cooled to room temperature and sample for dilatometry are made by

cutting the glass with the help of diamond cutter. Samples are undergone 1st stage heat treatment to make nucleation at the temperature of 850^{O}C for 2hour. After nucleation 2nd stage heat treatment is done for crystal growth which is called crystallization temperature. This crystallization is done at the temperature of 1250^{o}C with varying soaking time of 2, 4, 6 hour. By following the above procedure three sample are made by changing nucleating agents (TiO_2, ZrO_2, and TiO_2-ZrO_2).

CHAPTER 4

TESTING AND CHARACTERIZATION

[5.1] Chemical Analysis of rice husk ash silica by Hf method

1. Platinum crucible was taken and its weight was measure with digital weighing machine.
2. Little amount of rice husk ash silica was poured into the platinum crucible and its weight was taken.
3. 5-6 drop of water was added drop wise inside the crucible.
4. 8-9 drop of Sulfuric acid was added.
5. Then the crucible was filled with hydrofluoric acid.
6. After filling crucible was placed in the sand bath for 24 hours till the crucible became dry.
7. After drying the crucible was placed in a pit furnace till it become red hot.
8. In the final stage crucible was cool down and its weight was taken noted down.

[5.2] Bulk density and apparent porosity of cordierite based glass-ceramic

The apparent porosity and bulk density of the cordierite glass ceramic were determined by Archimedes principle using water. Dry Weight of the cordierite glass ceramic sample were measured and then the samples were put in water and boiled for about 2hour. After that suspended weight was measured using an apparatus in which suspended weight could be measured. After taking suspended weight, soaked weight is taken by cleaning water from the surface using tissue paper. Hence the dry weight, soaked weight and suspended weight were measured.

$$\text{Bulk Density} = \frac{\text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}}$$

$$\text{Apparent Porosity} = \frac{\text{Soaked Weight} - \text{Dry Weight}}{\text{Soaked Weight} - \text{Suspended Weight}}$$

[5.3] Phase analysis by XRD

The X-ray diffraction method was used for determining the phases in the cordierite glass-ceramic. The three different type of cordierite containing three different nucleating agent (TiO_2, ZrO_2 and TiO_2-ZrO_2) were cut into small rectangular pieces and then got ready to XRD for identification of the phases after nucleation and crystallization. XRD measurements are performed at an angle of 5-70^o with scanning speed of 10 °C/min using an X-ray Philips diffractometer with nickel filtered CuKα radiation (1.5406A^O) operated at 40 keV and 30 mA. The X- Ray data was plotted using the Expert Pro software and the peaks were matched with JCPDS software to get the phases present.

[5.4] Microstructure analysis by SEM

Microstructure of cordierite glass- ceramic were studied by using Scanning Electron Microscope (NOVA NANO SEM 450).It gives topological and elemental information at magnification of 1000x to 20000x and it has higher resolution than optical microscope. Polished samples were prepared with emery paper of grade P 400 ad P 600 untila plane and clear surface is attained. Then polished sample was ultrasonicated in acetone to clean the surface of the Sample. The polished samples were coated with palladium-platinum for 2-3 min to make the surface conducting. The specimens were observed by SEM in BSE and SE mode

[5.5] Measurement of linear thermal expansion coefficient

Linear thermal expansion coefficient was measured by using dilatometry. Cordierite based glass-ceramic were cut into rectangular shape and its dimension was measured. The equipment used was NETZSCH DL 402C Dilatometer with an operating range of 25-1600^{o}C.

The glass ceramic samples were put under test at a temperature range starting from room temperature to 1000^{o}C. The heating rate employed here was 10^{o}C per minute. .

Fig.1. High Temperature Dilatometer DIL 402C (NETZSCH)

[5.6] Mechanical properties measurement by Vickers hardness

Glass ceramic samples were polished and ultrasoncated with acetone to make surface clear for indentation. The hardness test was studied by a Vickers semi-macro hardness tester. The samples were indented by a diamond indenter with 49N and 98N load with 10seconds dwell time. The hardness of the materials was calculated from the size of the impression produced under load by a pyramid-shaped diamond indenter. The indenter used in the test is a square based pyramid whose opposite sides met at the apex at an angle of 136^{O}.The size of the impression (diagonals) was measured with the aid of a calibrated optical microscope (make ZEISS). The hardness of various samples was measured by using the formula.

$$H_v = 1.854(F/d^2)$$

F = Applied load in Kgf

D = Area of indentation in mm^2

CHAPTER 5

RESULTS & DISCUSSION

[6.1] Chemical analysis of rice husk ash silica

Crucible weight = 23.7861 gm; Sample weight =0.2103 gm.

Crucible + sample weight=23.9964 gm

After firing sample weight + Crucible weight =23.8012 gm

After firing sample weight = 23.8012 -23.7861=0.0151 gm

Impurities present = 0.2103-0.0151 = 0.1952 gm

$$\% \text{ of Purity} = \frac{0.1952}{0.2103} \times 100 = 92.81\%$$

Hence we got 92.81% pure silica from rice husk ash.

[6.2] Bulk density of cordierite glass-ceramics

1) Sample type	Bulk Density (gm/cm^3)	Apparent Porosity (%)
TiO_2 nucleated sample		
TiO_2(850 ^oC (2hr)-1250 ^oC (2hr))	2.49	0.034
TiO_2(850 ^oC (2hr)-1250 ^oC (4hr))	2.58	0.021
TiO_2(850 ^oC (2hr)-1250 ^oC (6hr))	2.65	0.017
TiO_2-ZrO_2 Mix nucleated sample		
TiO_2-ZrO_2(850 ^oC (2hr)-1250 ^oC (4hr))	2.58	0.018
TIO_2-ZrO_2(850 ^oC (2hr)-1250 ^oC (6hr))	2.70	0.0123
ZrO_2 nucleated sample		
ZrO_2(850 ^oC (2 hr) -1300 ^oC (4hr)	2.64	0.017
ZrO_2 (850 ^oC (2hr)-1350 ^oC (4hr)	2.65	0.019
ZrO_2(850 ^oC -1350 ^oC) (6hr)	2.66	0.018

Table-6 Bulk density of glass-ceramics sample measured by boiling water method

Table 6 shows the bulk density and apparent porosity of cordierite based glass ceramic prepared by three different nucleating agent (TiO_2, (TiO_2-ZrO_2) mix and ZrO_2) with varying temperature and soaking time of heat treatment.

Bulk density (B.D.) of all glass-ceramic samples were given in table -6 the difference in B.D. value while composition is been changed is evident from that tabulation. Samples containing TiO_2 show an increasing trend in the bulk density value with increasing duration of heat-treatment. This is due to crystal growth in expense of glass matrix. When ZrO_2 was used as nucleating agent, B.D. values were obtained as higher than the glass-ceramics containing only TiO_2. This thing could be due to formation of dense glass with ZrO_2.

[6.3] Phase analysis and microstructure of cordierite glass ceramics

6.3.1 X-ray diffraction analysis

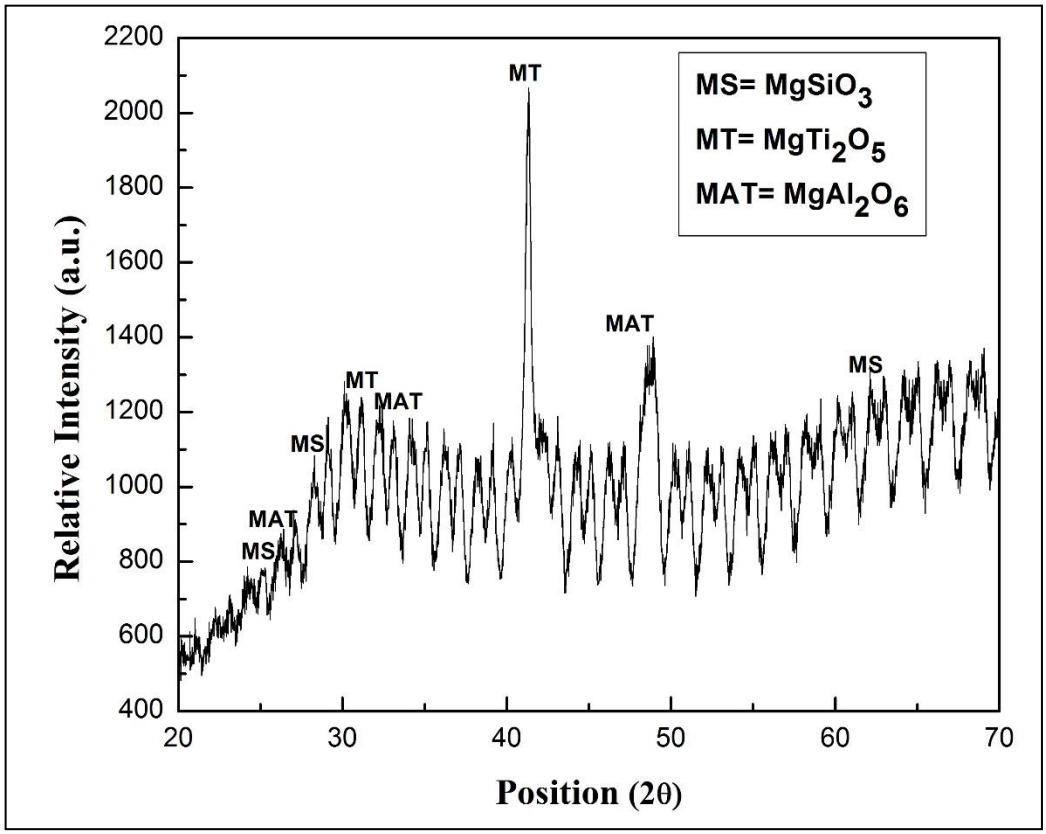


Fig.2 XRD pattern of TiO_2 nucleated cordierite glass-ceramic heat treated at 850^oC for 2 hour soaking period.

The X-ray diffraction was represented at figure 2 for the TiO_2 nucleated at 850 ^oC for 2 hour. It was observed that there are many broad peaks with insignificant intensity present in the sample. That suggests the nucleation phenomenon was started at 850^oC. The major crystalline phases were identified as i) magnesium silicate ($MgSiO_3$, known as enstatite), ii) magnesium titanate ($MgTiO_3$) and iii) magnesium aluminium titanate ($MgAl_2TiO_6$). The following abbreviations were used at two theta positions corresponding to highest intensity peaks.

Phase name with abbreviation	2θ position (degree)	Remark
Magnesium silicate ($MgSiO_3$) [MS]	25.1, 28.3 and 62	Highest intensity at 28.3 degree
Magnesium titanate ($MgTiO_3$) [MT]	31.24, and 41.35	Highest intensity at 41.35 degree
Magnesium aluminium titanate ($MgAl_2TiO_6$) [MAT]	26.28, 33.13 and 47.8	Highest intensity at 33.13 degree

Table 7- shows the phases & position of TiO_2 nucleated cordierite glass-ceramic heat treated at 850^{o}C for 2 hour soaking period.

The X-ray diffraction of the glass-ceramic thus reveals the presence of finely crystalline phases which are supposed to play the role of primary crystal phase in the crystal growth stage.

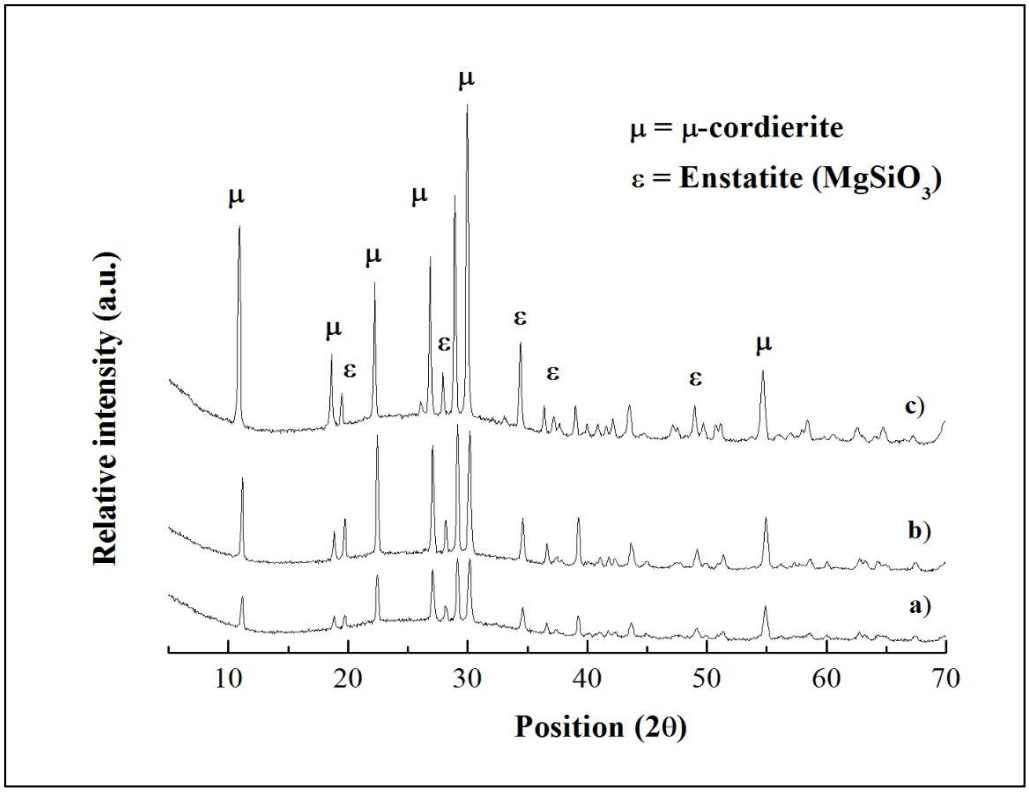


Fig.3 XRD pattern of TiO_2 nucleated cordierite glass ceramic heat treated at three different soaking period a) 850^{o}C (2hr)-1250^{o}C (2hr), b) 850^{o}C (2hr)-1250^{o}C (4hr), c) 850^{o}C (2hr)-1250^{o}C (6hr), Only μ-cordierite along with some amount of enstatite were identified to be present as represented by figure 3

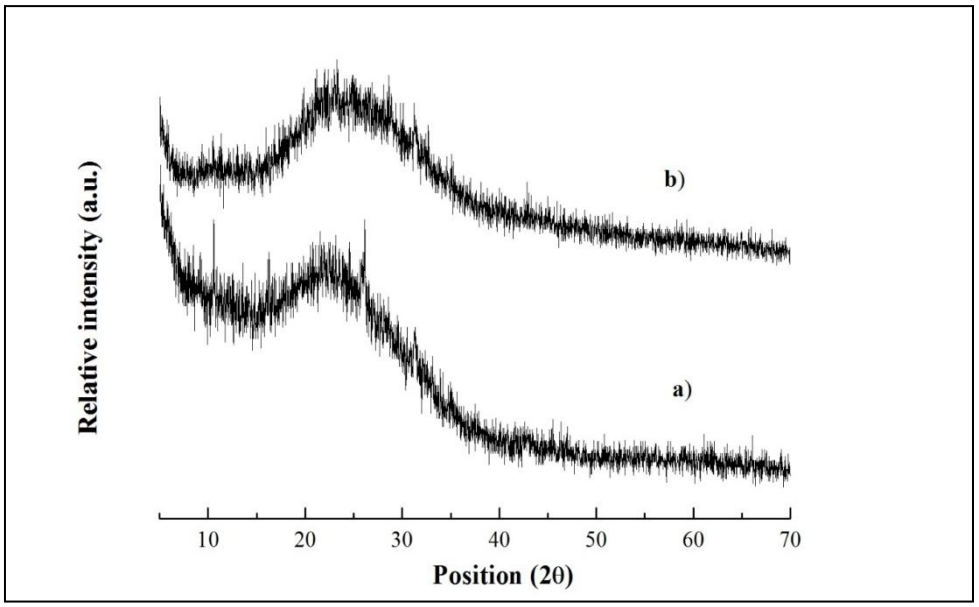


Fig.4. XRD pattern of TiO_2 and ZrO_2 (mix) nucleated cordierite glass ceramic heat treated at different soaking period. a) 850 ^oC (2hr)-1250 ^oC (4hr), b) 850 ^oC (2hr)-1250 ^oC (6hr).

As the figure 4 shows the samples containing both TiO_2 and ZrO_2 as nucleating agent are amorphous even after the heat treatment at 1250 ^oC for 6 hour.

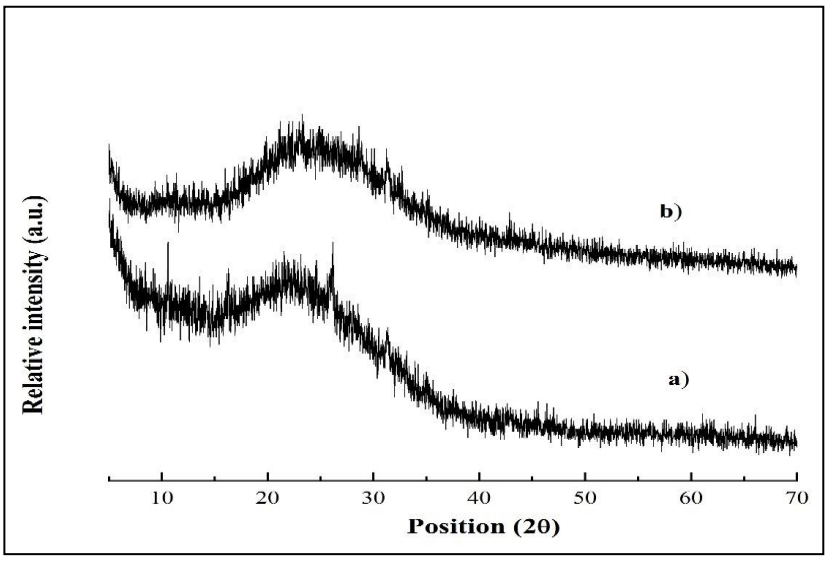


Fig.5. XRD pattern of and ZrO_2 nucleated cordierite glass ceramic heat treated at different soaking period. a) 850^oC (2hr)-1350 ^oC (4hr), b) 850^oC (2hr)-1350 ^oC (6hr).

The samples containing only ZrO_2 as nucleating agent is mainly amorphous as evident from the figure 5 it could be assumed that the ultrafine crystallites are present in trace amount below 4.0 % by volume.

[6.3.2] Microstructure analysis of cordierite glass-ceramic

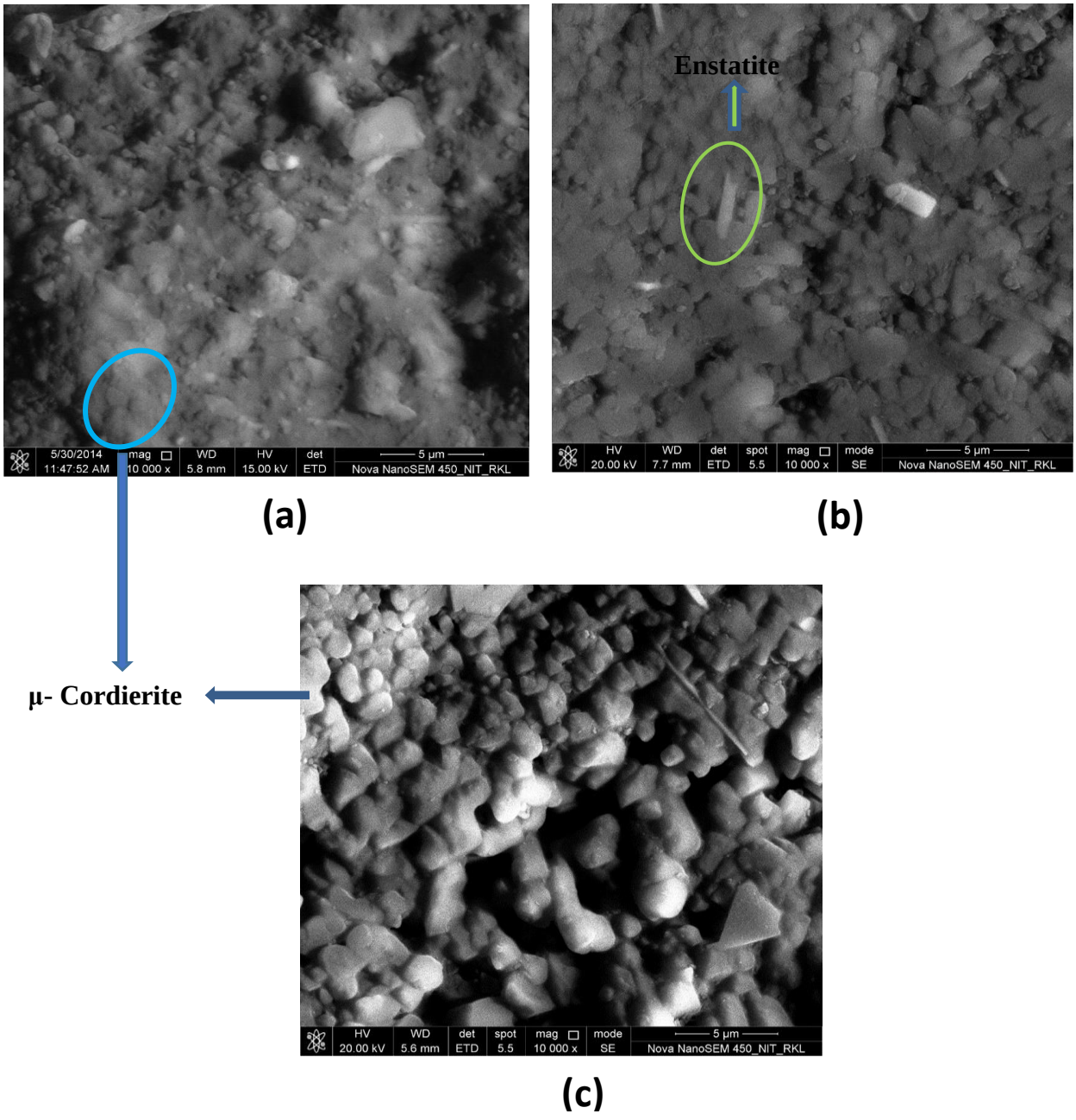
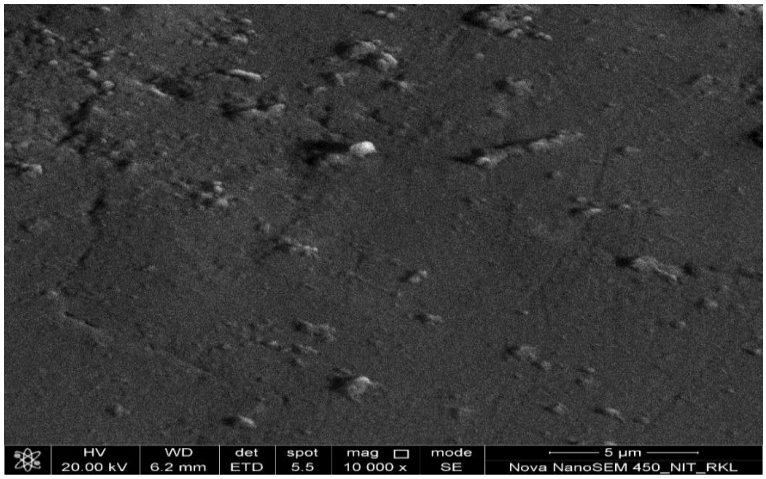
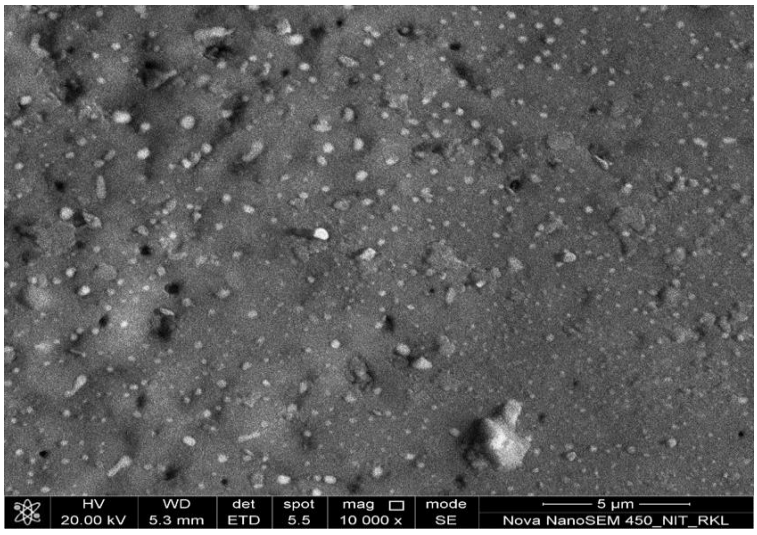


Figure - 6 SEM image of TiO_2 nucleated cordierite glass-ceramic heat treated for nucleation at 850 ^{O}C for (2hr) + 1250 ^{O}C with three different soaking period of a) 2hr, b) 4hr and c) 6hr.

The phases of different morphology sample containing TiO_2 as nucleating agent were identified and marked in the figure 6 and those are tabulated below. The crystal growth data at varying time (soaking time) was also given in that table 8. It could be concluded that there are no major morphological changes while increasing the soaking time at temperature 1250^{o}C.



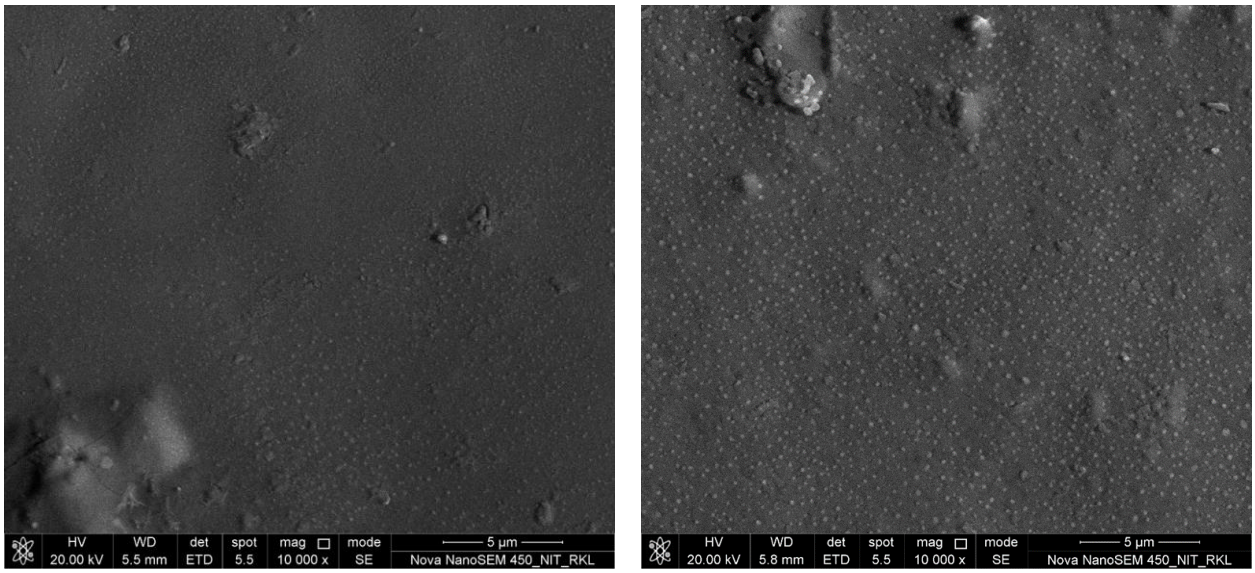
(a)



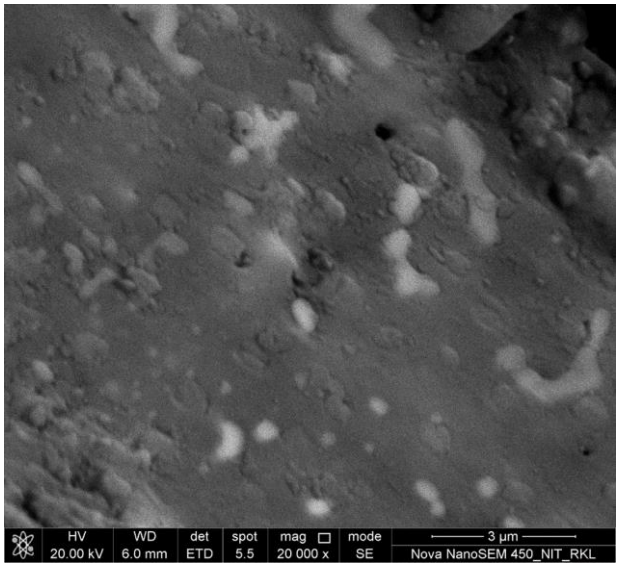
(b)

Figure – 7 SEM image of TiO_2-ZrO_2 (mix) nucleated cordierite glass-ceramic heat treated for nucleation at 850 ^{O}C for 2hr +1250 ^{O}C with three different soaking period of a) 2hr, b) 4hr and c) 6hr.

Figure 7 represents the development of phases in the glassy matrix of samples containing (TiO_2+ZrO_2) as nucleating agent. The significant thing to observe is that only a few crystals of submicron sized are developed. The distribution of grains in the glass matrix is homogeneous. Average grain size ranges from 0.16 to 0.266 μm.



(a) **(b)**



(c)

Figure -8 SEM image of ZrO_2 nucleated cordierite glass-ceramic heat treated for nucleation at 850 ^{O}C for 2hr+1250 ^{O}C with three different soaking period of a) 2hr, b) 4hr and c) 6hr.

Figure 8 depicts the microstructure of the samples containing ZrO_2 as nucleating agent. The microstructural information was tabulated below.

Sample type	Morphological identification	Average crystal size
TiO_2 nucleated samples		
(850(2hr)-1250(2hr))	µ-cordierite – prismatic structure	0.473 micron (µ cordierite)
(850(2hr)-1250(4hr))	µ-cordierite – prismatic (pseudo hexagonal-prism) Enstiatite- dipyramidal	0.668 micron (µ-cordierite),enstiatite
(850(2hr)-1250(6hr))	µ-cordierite – prismatic structure Enstiatite- dipyramidal	1.29 micron (µ-cordierite)
(TiO_2-ZrO_2) mix nucleated samples		
(850(2hr)-1250(4hr))	Very small sized magnesium aluminium titanate and magnesium aluminium zirconate nuclei are formed.	0.160 micron
(850(2hr)-1250(6hr))	Growth of nuclei occurs.	0.266 micron
ZrO_2 nucleated samples		
(850(2hr)-1300(4hr))	Very small size magnesium aluminium zirconate nuclei are formed.	0.107 micron
(850(2hr)-1350(4hr))	Magnesium aluminium zirconate nuclei are formed.	0.171 micron
(850(2hr)-1350(8hr))	Magnesium aluminium zirconate nuclei occurs	0.251 micron

Table – 8. Morphological identification and average grain size of cordierite based glass ceramic prepared by three different nucleating agent (TiO_2, (TiO_2-ZrO_2) mix and ZrO_2) with varying temperature and soaking time of heat treatment.

[6.5] Linear thermal expansion of cordierite glass ceramic

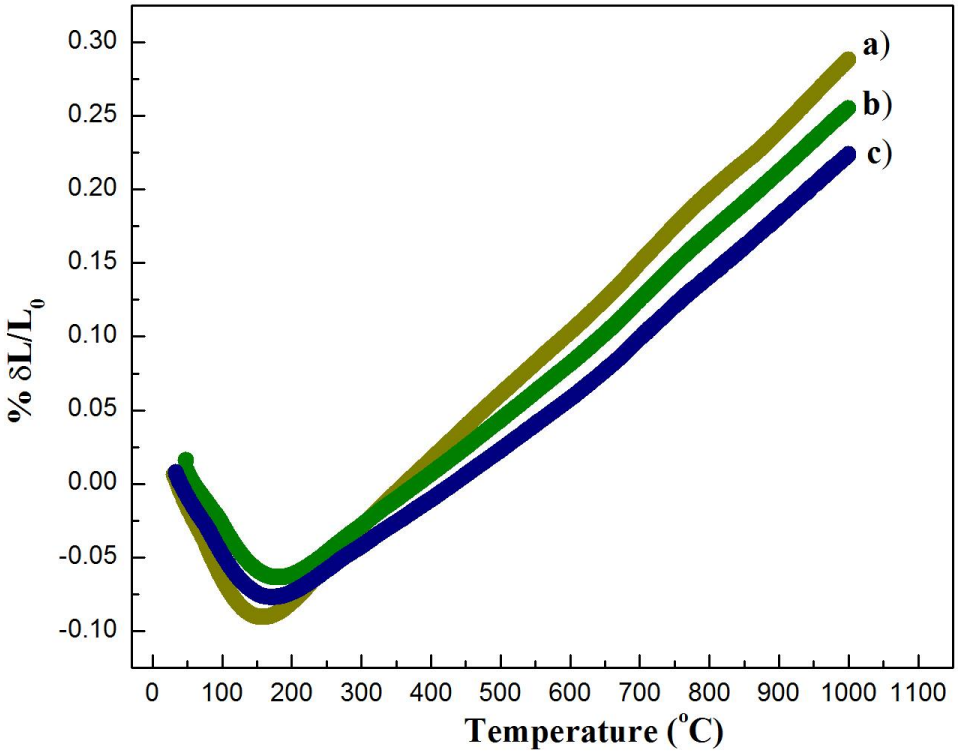


Fig.-9. Linear thermal expansion coefficient of TiO_2 nucleated cordierite glass ceramic heat treated for nucleation at 850 ^{O}C for 2 hour + 1250 ^{O}C with different soaking period as 2, 4 and 6 hour for a) , b) and c) respectively.

From the figure 9 it was observed that all glass-ceramic samples have two different thermal co-efficient of expansion value (TCE). Table 9 represents the TCE values along with corresponding different zone of temperature. One of the reasons behind the negative expansion co-efficient could be the anisotropic expansion of μ-cordierite (appeared as major crystalline phase) in these kind of samples (TiO_2 as nucleating agent). The expansion of the samples were found to decrease with increasing heat-treatment duration (second stage 2 to 6 hour). This is due to the increasing volume percentage of crystalline phases in the parent glassy matrix.

Sample type	Thermal co-efficient of expansion		Transition zone of Temperature
	Zone-1	Zone-2	
(a) sample heat-treated at 850/2hr + 1250/2hr (TiO_2 only)	-9.395×10^{-6} /°C (27–140 °C)	4.536×10^{-6} /°C (175 - 1000 °C)	140 to 175 °C
(b) sample heat-treated at 850/2hr + 1250/2hr (TiO_2 only)	-7.182×10^{-6} /°C (27 – 165 °C)	4.038×10^{-6} /°C (200-1000 °C)	165 to 200 °C
(c) sample heat-treated at 850/2hr + 1250/2hr (TiO_2 only)	-7.745×10^{-6} /°C (27-150 °C)	3.76×10^{-6} /°C (190 – 1000 °C)	150 to 190 °C

Table 9 shows thermal expansion coefficient and transition zone of temperature of TiO_2 nucleated glass ceramic prepared by varying temperature and soaking time of heat treatment.

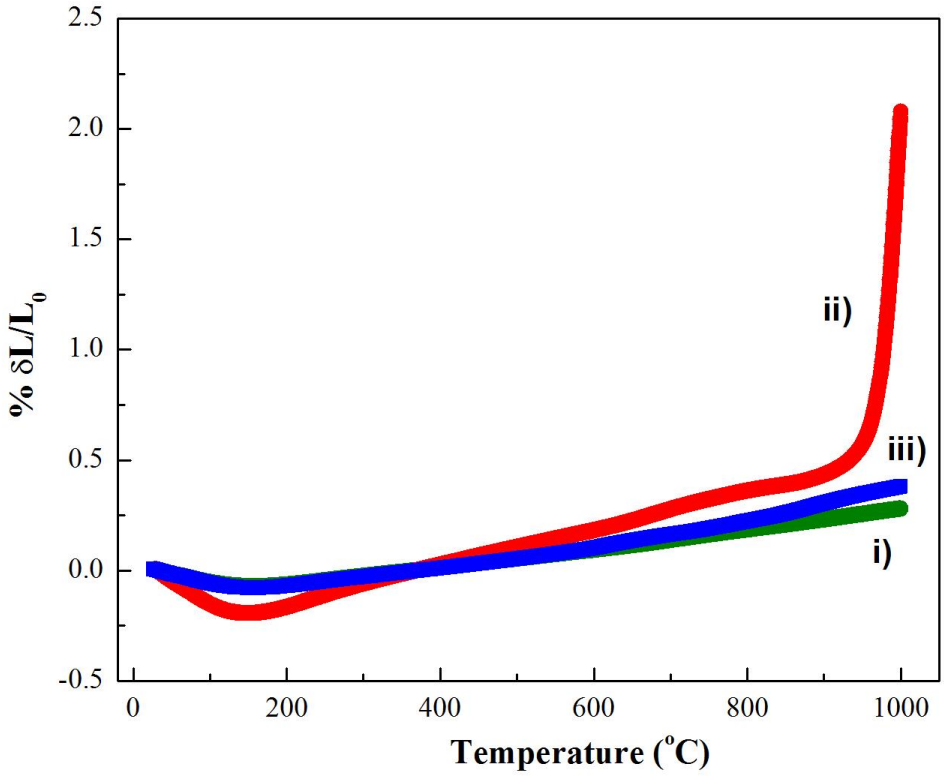


Fig.-10. Linear thermal expansion coefficient of cordierite glass ceramic nucleated with three different nucleating agent i) TiO_2-ZrO_2(mix), ii) TiO_2 iii) ZrO_2. All samples were heat treated at 850 °C for 2 hour (first stage) and 1250 °C for 4 hour (second stage) for (TiO_2 and TiO_2-ZrO_2 (mix)) and 1350 °C for ZrO_2 containing sample.

When thermal expansion behavior were compared among the glass-ceramics containing different nucleating agent, clearly two distinct zone appeared to represent two different thermal co-efficient value except for glass-ceramic sample containing ZrO_2 only. The sharp rise of the expansion curve after 870 ^oC for the glass-ceramic sample containing mix (TiO_2 + ZrO_2) was observed. This is possibly due to the softening of glass matrix. The single valued thermal co-efficient of expansion may be due to the property of B_2O_3 modified magnesium aluminosilicate glass. This glass-ceramic exhibits low expansion.

Sample type	**Thermal co-efficient of expansion**		**Transition zone of temperature**
	Zone-1	**Zone-2**	
i) Glass-ceramic of the heat-treatment 850/2hr + 1250/4hr (TiO_2)	-7.813×10^{-6} /^oC (27 – 130 ^oC)	4.297×10^{-6} /^oC (185 – 1000 ^oC)	130 to 185 ^oC
ii) Glass-ceramic of the heat-treatment 850/2hr + 1250/4hr (TiO_2-ZrO_2) mix	-6.575×10^{-6} /^oC (27 – 130 ^oC)	8.334×10^{-6} /^oC (178 – 1000 ^oC)	130-178 ^oC
iii) Glass-ceramic of the heat-treatment 850/2hr + 1350/4hr (ZrO_2)	-8.497×10^{-6} ^oC (27-150 ^oC)	4.45×10^{-6} /^oC (170 – 1000 ^oC)	150 – 170 ^oC

Table 10 thermal expansion coefficient and transition zone of temperature of glass ceramic prepared by three different nucleating agent (TiO_2, (TiO_2-ZrO_2) mix and ZrO_2) with varying temperature and soaking time of heat treatment.

[6.6] Vickers's hardness for cordierite glass ceramic

Sample type	Hardness (GPa)
TiO_2 nucleated sample	
TiO_2(850 ^oC (2hr)-1250 ^oC (2hr))	4.332
TiO_2(850 ^oC (2hr)-1250 ^oC (4hr))	5.035
TiO_2(850 ^oC (2hr)-1250 ^oC (6hr))	6.226
TiO_2-ZrO_2 Mix nucleated sample	
TIO_2-ZrO_2(850 ^oC (2hr)-1250 ^oC (6hr))	4.319
ZrO_2 nucleated sample	
ZrO_2(850 ^oC -1350 ^oC) (6hr)	6.059

Table 11 Vickers hardness of glass ceramic prepared by three different nucleating agent (TiO_2, (TiO_2-ZrO_2) mix and ZrO_2) with varying temperature and soaking time of heat treatment.

The table 11 represents the hardness measured by Vickers indentation method. The range of data values suggests that samples are moderately high hard. The possibility of obtaining much more hardness value remains in the ability to develop much more crystalline phases in the glass matrix.

CHAPTER 6

CONCLUSION

CONCLUSION

1. At 1250 ^{o}C, μ-cordierite is able to grow in TiO_2 containing glass ceramic sample along with a few amount of enstatite.

2. To obtain α-cordierite (higher form) sample should undergo more than 1250 ^{o}C for heat treatment.

3. Glass ceramic which contain TiO_2+ ZrO_2 or only ZrO_2, (850 ^{o}C) is not enough to nucleate much number of embryos. So heat treatment is needed with modified schedule.

4. If composition is properly designed, the negative thermal co-efficient of expansion of glass-ceramic sample could be exploited to develop ceramics with virtually ‘zero thermal coefficient of expansion.

5. Hardness value could be increased in the glass-ceramics using ZrO_2 only as nucleating agent.

CHAPTER 7

REFERENCES

REFERENCES

1. "A novel process for the synthesis of cordierite ($Mg_2Al_4Si_5O_{18}$) powders from rice husk ash and other sources of silica and their comparative" study by Milan Kanti Naskar, Journal of the European Ceramic Society 24 (2004) 3499–3508

2. "Effects of (B_2O_3, P_2O_5) Additives on Microstructural Development and Phase-Transformation Kinetics of Stoichiometric Cordierite Glasses". Jenn-Ming Wu and Shiang-Po Hwang. J. Am. Ceram. Soc., 83 [5] 1259–65 (2000)

3. "Crystallization behavior and sintering of cordierite synthesized by an aqueous sol–gel route". By Rada Petrovic´ Ceramics International 38 (2012) 1835–1841

4. "Sintering Additives to Eliminate Interphases in Cordierite Ceramics" Zhi Ming Shiw J. Am. Ceram. Soc., 88 [5] 1297–1301 (2005)

5. "The Effect of Manganese Doping on the Mechanical Behavior of Cordierite Glass-Ceramics". Yu. V. Baschenko. Journal of the European Ceramic Society, 8 (1991) 181 - 185

6. "Sintering, crystallization and properties of $MgO–Al_2O_3–SiO_2$ system glass-ceramics containing ZnO" Guo-Hua Chena, Journal of Alloys and Compounds 431 (2007) 282–286

7. "Optimization of parameters for aqueous tape-casting of cordierite-based glass ceramics by Taguchi method". Jose´ Maria F. Ferreira Materials Science and Engineering A334 (2002) 11–18

8. "Cordierite-based glass-ceramics processed by slip casting" J.M.F Ferreira Journal of the European Ceramic Society 21 (2001) 185-193

9. "The reaction kinetics of rice husk based cordierite ceramics" S. Kurama Ceramics International 34 (2008) 269–272

10. "Low-Temperature Fabrication of Cordierite Ceramics from Kaolinite and Magnesium Hydroxide Mixtures with Boron Oxide Additions" Yuichi Kobayashi and Etsuro Kato J. Am. Ceram. Soc., 82 [3] 783–85 (1999)

11. "Synthesis, characterization and sintering behavior influencing the mechanical, thermal and physical properties of cordierite-doped TiO_2" Senthil Kumar Marikkannana j mater res technol. 2013; 2(3):269–275

12. "Processing of cordierite based ceramics from alkaline-earth aluminosilicate glass, kaolin, alumina and magnesite" J.A. Labrinchad Journal of the European Ceramic Society 22 (2002) 1775–1782

13. "Crystallization of non-stoichiometric cordierite glasses". M.A. Camerucci Ceramics International 31 (2005) 189–195

14. "Sintering and crystallization behavior of chemically prepared cordierite for application in electronic packaging" S. Mukhopadhyay Ceramics International 30 (2004) 1067–1070

15. "Microstructural Evolution in Fast-Heated Cordierite-Based Glass-Ceramic Glazes for Ceramic Tile" Francisco Jose Torres and Javier Alarco´n *J. Am. Ceram. Soc.*, 87 [7] 1227–1232 (2004)

16. "Densification and properties of glass/cordierite composites" M.F. Zawrah Ceramics International 31 (2005) 383–389